

Amorphous Ta-Si-N thin-film alloys as diffusion barrier in Al/Si metallizations

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Amorphous Ta-Si-N thin films of a wide range of compositions were prepared by rf reactive sputtering of a Ta₅Si₃ target in a N₂/Ar plasma. The relationship between films' composition and resistivity is reported. All obtained films were tested as diffusion barriers between Al and Si. Backscattering spectrometry combined with cross-sectional transmission electron microscopy were used to determine the barrier effectiveness. It was found that aluminum can be melted on top of the Si/Ta-Si-N structure (675 °C for 30 min) without any evidence of metallurgical interactions between the layers.

I. INTRODUCTION

The fabrication of stable, reproducible, and uniform contacts is essential for successful device performance. In silicon integrated circuits, aluminum is commonly used for contacts and interconnections, but a severe degradation of contacts is caused by intermixing and reactions between aluminum and silicon. To minimize such deleterious interactions, diffusion barriers are used in very large scale integrated (VLSI) contact technologies.¹⁻³ Various interstitial alloys such as nitrides,⁴⁻⁹ carbides,¹⁰⁻¹¹ borides,¹² conductive oxides,¹³⁻²⁰ and amorphous alloys²¹⁻²⁷ have been investigated as diffusion barriers in contact metallizations. Because they lack grain boundaries that can act as fast diffusion paths, amorphous alloys are an attractive alternative to polycrystalline thin films. Until now, the stability of these amorphous alloy films, when in contact with the substrate or metal layers, has been limited by the tendency of these alloys to react with the metal overlayers or with the substrate rather than by the crystallization of the amorphous films.²⁰⁻²³ Thus, the choice of elements which form an amorphous diffusion barrier is very important. For example, binary amorphous alloys formed by two transition metals are not effective diffusion barriers between Al and Si. For these amorphous alloys, the formation of compounds between one or both of the barrier elements and Al or Si far below their crystallization temperatures is the primary failure mechanism.²¹⁻²⁵ Interstitial alloys in amorphous form are another type of diffusion barrier^{8,9,14} tested previously. In general, their chemical stability with Al and Si is superior, but they usually lose their effectiveness due to interdiffusion of Al and Si which occurs through localized weak spots that are always present. Even though it seems logical that amorphous alloys should be more effective diffusion barriers than their polycrystalline counterparts, clear evidence in support of this idea still does not exist in literature.

We report on properties of amorphous Ta-Si-N alloys as diffusion barriers between Al and Si. Backscattering spectrometry and cross-sectional transmission electron micrographs (XTEM) have been used to determine the stability of amorphous Ta-Si-N films interposed between a (Si) substrate and an Al overlayer (Si/Ta-Si-N/Al).

II. EXPERIMENTAL PROCEDURE

Substrates of (111) oriented *n*-type Si of 0.005 Ω cm resistivity were used throughout this experiment. To study the

crystallization temperature of amorphous Ta-Si-N alloy, films were deposited on (100) Al₂O₃ substrates. Prior to loading into the deposition chamber, the silicon wafers were etched with diluted HF. The Al₂O₃ substrates were cleaned ultrasonically with trichloroethanol (TCE), acetone, and methanol, and then blown dry with nitrogen. All depositions were performed in an rf sputtering system equipped with a cryopump and a cryogenic baffle. The sputtering chamber was evacuated to a base pressure of about 5×10^{-7} Torr before deposition. A magnetron-type circular cathode, 7.5 cm in diameter was used as the sputtering source. The substrate holder was placed about 7 cm below the target and was neither cooled nor heated externally.

The Ta-Si-N films were deposited by reactive sputtering of a Ta₅Si₃ target in an Ar/N₂ gas mixture. The flow ratios of Ar to N₂ and total gas pressure were adjusted by mass flow controllers and monitored with capacitive manometer in a feedback loop. All Ta-Si-N films were sputtered with 10 mTorr total gas pressure and 300 W forward sputtering power. The ratio of nitrogen to argon gas flow was in the range of 0% to 5.3%. Negative dc bias was applied to the substrate holder during some depositions. The aluminum overlayer was sputter-deposited in pure argon (5 mTorr pressure) on top of the Si-Ta-N films without breaking vacuum.

The composition of the Ta-Si-N films as well as the amount of impurities was derived from backscattering spectra of these films deposited on carbon. X-ray diffraction together with electron transmission microscopy were used to determine a microstructure and crystallographic structure of the films. The electrical resistivities of the films were obtained from sheet resistance measurements with a four-point probe. Backscattering spectrometry and XTEM were used to evaluate the diffusion barrier capability of the Ta-Si-N films metallization. Annealing of the samples was carried out in a vacuum of better than 1×10^{-6} Torr in the temperature range of 500–675 °C for different annealing durations.

To prepare samples for XTEM of the contact structures, the samples were first glued together face to face, followed by mechanical thinning to 10 μm. Finally, argon ion milling at liquid nitrogen temperature was used to thin the specimen to electron transparency.

III. RESULTS AND DISCUSSION

The atomic composition of the Ta-Si-N films was determined by backscattering spectrometry of the samples depos-

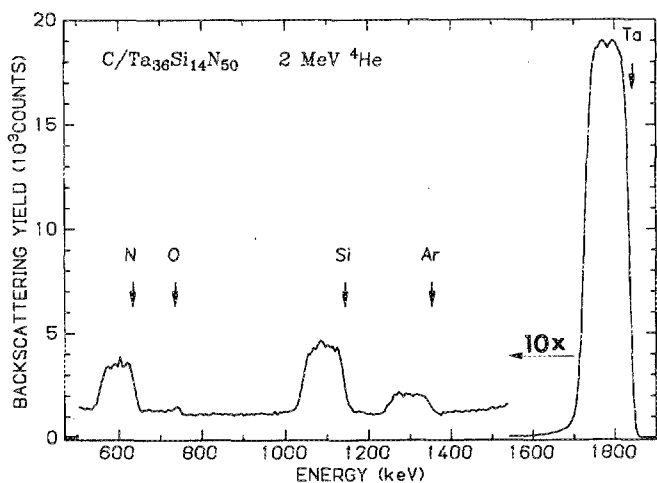


FIG. 1. 2 MeV ^4He backscattering spectrum of the $\text{C}/\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ sample.

ited on carbon. Figure 1 shows the backscattering spectrum of a $\text{C}/\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ sample about 120 nm thick. There is about 3 at. % of argon and 3 at. % of oxygen incorporated into these films as impurities. This impurity level is typical for films of all compositions. Figure 2 shows the composition of Ta-Si-N films as a function of the nitrogen-to-argon flow ratio in the sputtering chamber. It is immediately noticeable that increased nitrogen levels can be incorporated in the films when the nitrogen/argon flow ratio rises. The nitrogen content in the films increases continuously from 0% to 64% as the N_2/Ar flow ratio changes from 0% to 11%. There is no sharp transition in the nitrogen concentration of the Ta-Si-N films over the whole range of the N_2/Ar flow ratios investigated. Figure 3 shows the resistivity of Ta-Si-N films as a function of their composition. Resistivity of a pure 120 nm thick $\text{Ta}_{74}\text{Si}_{26}$ film is about 265 $\Omega\text{ cm}$ and rises slowly to 625 $\Omega\text{ cm}$ as the composition of the film reaches $\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$. Further increase in nitrogen concentration causes a rapid

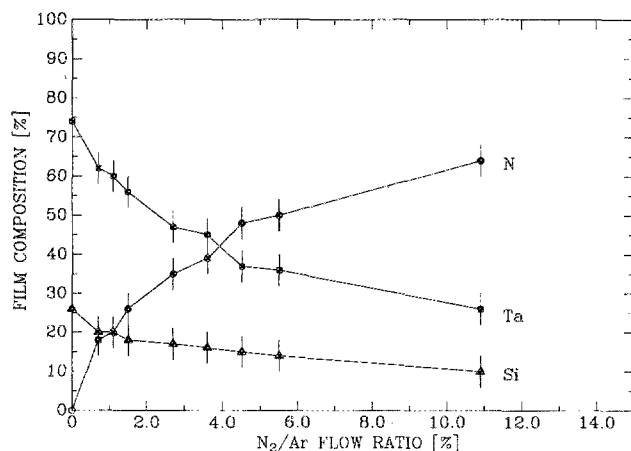


FIG. 2. The composition of Ta-Si-N films as a function of the N_2/Ar flow ratio.

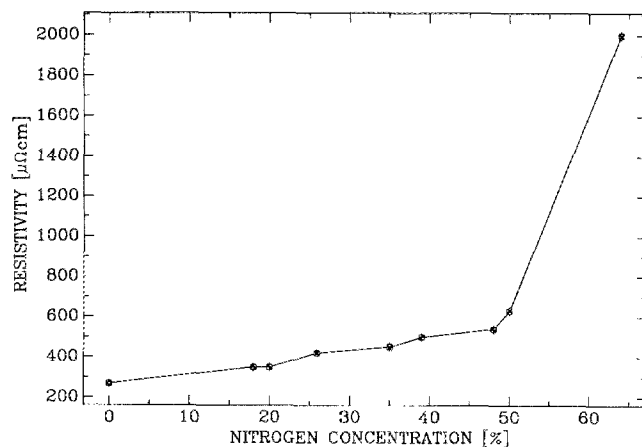


FIG. 3. The resistivity of Ta-Si-N films is a function of the N_2/Ar flow ratio.

increase in the resistivity. A $\text{Ta}_{26}\text{Si}_{10}\text{N}_{64}$ film has about 4100 $\Omega\text{ cm}$. All films reported in this paper including $\text{Ta}_{74}\text{Si}_{26}$ were amorphous as deposited. Figure 4 shows the microstructure and diffraction patterns of the $\text{Ta}_{74}\text{Si}_{26}$ and

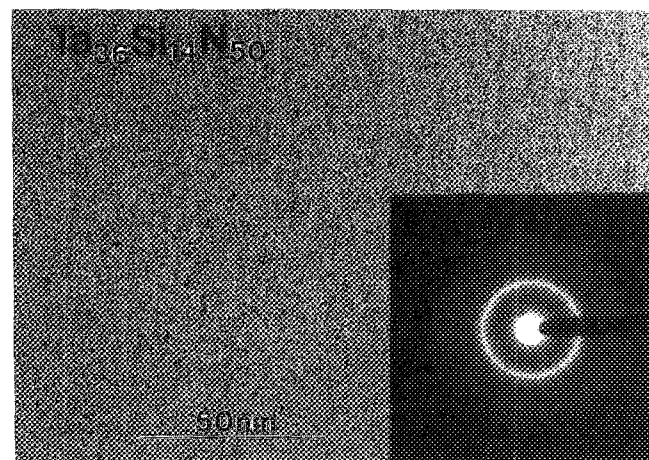
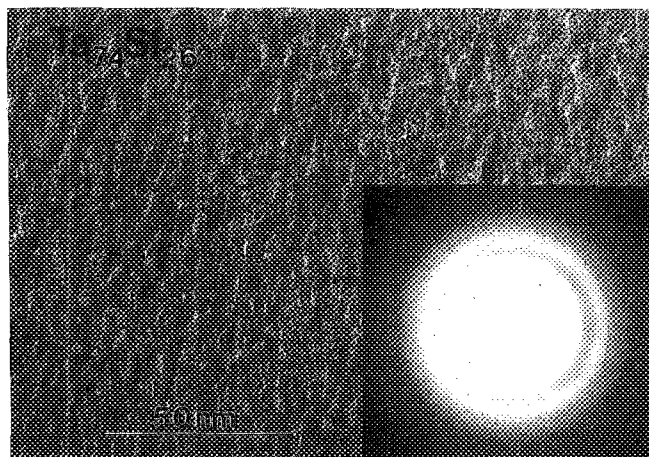


FIG. 4. TEM micrographs and diffraction patterns of the $\text{Ta}_{74}\text{Si}_{26}$ and $\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ thin films.

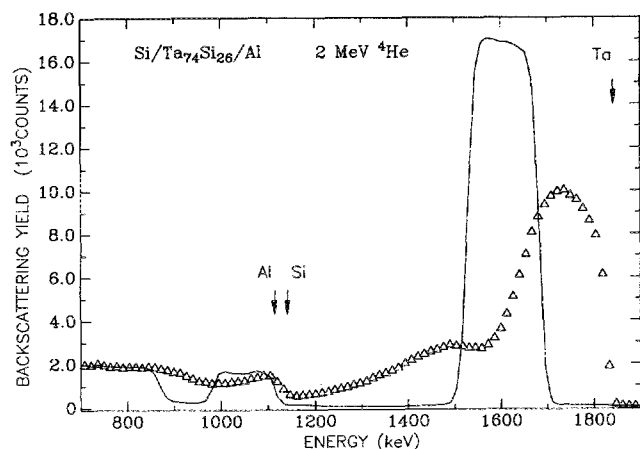


FIG. 5. 2 MeV ^4He backscattering spectra of the $(\text{Si})/\text{Ta}_{76}\text{Si}_{24}/\text{Al}$ test structure before and after annealing at 550 °C for 30 min (Δ); as-deposited (—).

$\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ films, respectively. The lack of grains in both micrographs together with the presence of one diffused ring in their diffraction patterns reveal the amorphous structure of both films. To determine the crystallization temperature, $\text{Ta}_{60}\text{Si}_{20}\text{N}_{20}$ and $\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ films deposited on an Al_2O_3 substrate were annealed in vacuum from 600 to 1100 °C for 60 min and examined on an x-ray Read camera. After annealing at 1100 °C, the diffraction rings associated with an amorphous structure were still present in the diffraction pattern but also three additional, extremely weak, broad, lines appeared in the pattern. Our effort to identify them have remained unsuccessful to date. According to the Ta-Si-N ternary phase diagram determined at 1327 °C by Brewer *et al.*²⁸ there exist a ternary Ta-Si-N phase in a certain range of composition $\text{Ta}_{5-x}\text{Si}_{3-y}\text{N}_2$. This ternary phase is stable below 1840 °C; at higher temperatures TaSi_2 equilibrates in a stable manner with nitrogen gas and all compounds, except TaSi_2 , decompose. Crystallographic data on the ternary

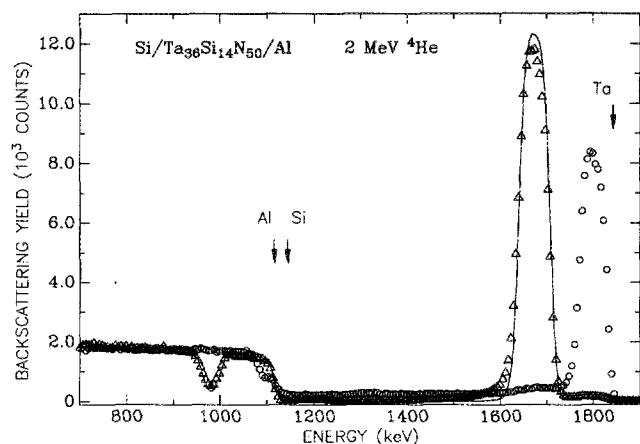


FIG. 6. 2 MeV ^4He backscattering spectra of the $(\text{Si})/\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ (60 nm)/Al (300 nm) test structure before and after annealing at 650 (Δ) and 675 °C (\circ) for 30 min. As deposited (—).

Ta-Si-N phase are not available in literature. In our study, three films. ($\text{Ta}_{60}\text{Si}_{20}\text{N}_{20}$, $\text{Ta}_{56}\text{Si}_{18}\text{N}_{26}$, and $\text{Ta}_{47}\text{Si}_{17}\text{N}_{35}$) are in the composition range of ternary phase.

All Ta-Si-N films reported in this paper (Fig. 2) were tested as diffusion barriers between Al and Si using backscattering spectrometry for failure detection. Figure 5 shows backscattering spectra of a nitrogen-free $(\text{Si})/\text{Ta}_{76}\text{Si}_{24}/\text{Al}$ sample before and after annealing at 550 °C for 30 min. It is clear that barrier, approximately 80 nm thick, fails after annealing. The presence of TaAl_3 was detected in the sample by x-ray diffraction. Nitridation of tantalum silicide drastically increases the stability of the barriers. Ta-Si-N films (about 600 nm thick) with nitrogen concentration from 18% to 26% prevent interactions between Al and Si temperatures up to 550 °C for 30 min heat treatments (failure temperature \approx 600 °C). $\text{Ta}_{47}\text{Si}_{17}\text{N}_{35}$ and $\text{Ta}_{45}\text{Si}_{16}\text{N}_{39}$ films were stable up to 600 °C for 30 min (failure was observed at 650 °C at 30 min). The best diffusion barriers were formed by $\text{Ta}_{37}\text{Si}_{15}\text{N}_{48}$ and $\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$. Both of them prevent an intermixing between Al and Si up to 650 °C. Further increase of nitrogen concentration in the films does not improve their

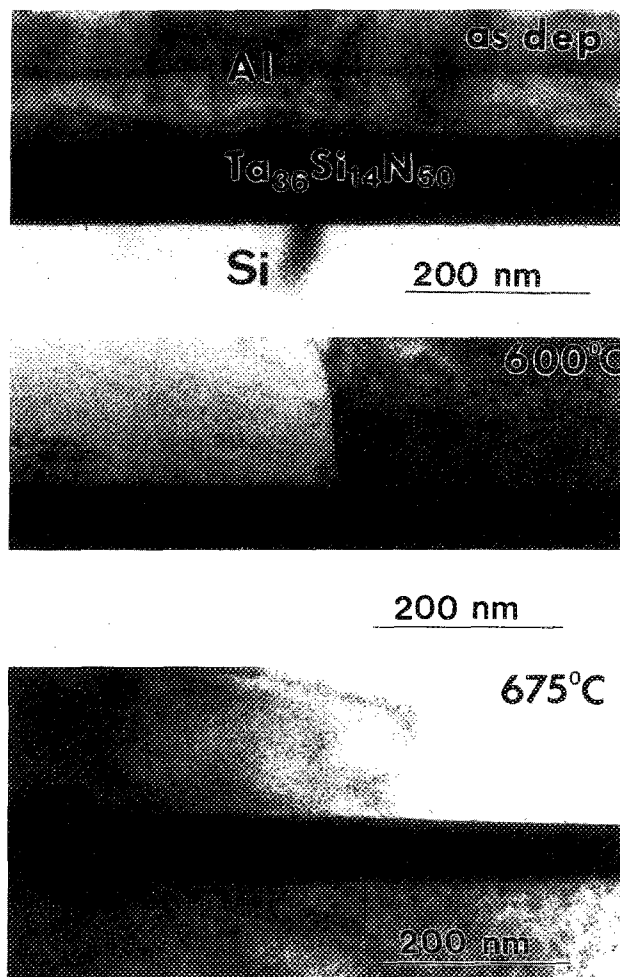


FIG. 7. XTEM micrograph of the as-deposited and annealed at 600 and 675 °C for 30 min $(\text{Si})/\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}/\text{Al}$ sample.

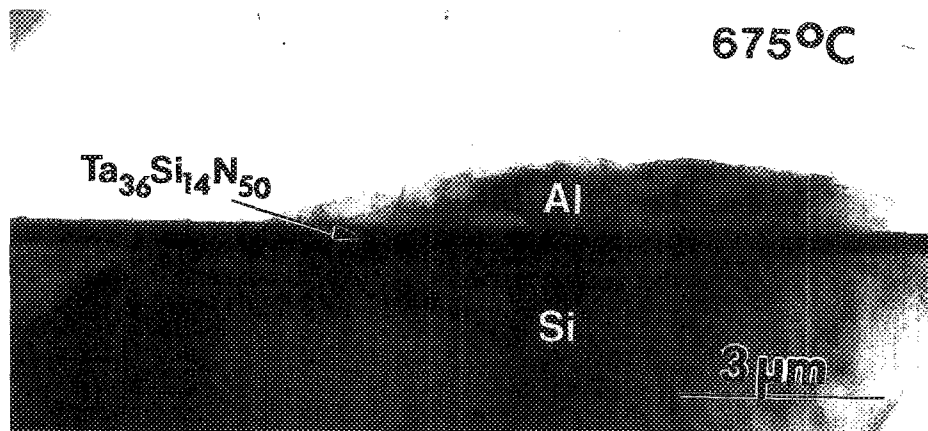


FIG. 8. XTEM micrograph of the $\langle\text{Si}\rangle/\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}/\text{Al}$ structure annealed at 675 °C for 30 min.

performance as diffusion barriers. A $\text{Ta}_{26}\text{Si}_{10}\text{N}_{64}$ film is effective only up to 600 °C. Figure 6 shows backscattering spectra of the $\langle\text{Si}\rangle/\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ (60 nm)/Al (300 nm) sample before and after annealing at 650 and 675 °C for 30 min. As can be seen there is no difference between the spectra of the as-deposited and 650 °C annealed samples. It means that within the resolution limit of backscattering spectrometry the Al and Si layers do not metallurgically interact during annealing. The spectrum after annealing at 675 °C (above the melting point of Al at 660 °C) indicates that the sample is laterally nonuniform. Aluminum no longer covers the whole surface of the sample because it coalesces at that temperature. This is also confirmed by optical microscopy. The x-ray diffraction pattern of the same sample indicates that the $\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ film remains amorphous. Unlike the case of the $\langle\text{Si}\rangle/\text{Ta}_{76}\text{Si}_{24}/\text{Al}$ sample annealed at 550 °C, no aluminides were detectable in the $\text{Si}/\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}/\text{Al}$ samples after annealing at 650 and 675 °C. Only very weak, TaSi_2 lines appeared in the diffraction pattern of these samples.

The cross-sectional structure of a $\langle\text{Si}\rangle/\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}/\text{Al}$ sample as-deposited, and annealed at 600 or at 675 °C for 30 min is shown in Fig. 7. The $\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ layer is amorphous

and has not crystallized after annealing at 675 °C. The structure of the sample annealed at 600 °C is identical to that prior to the heat treatment, except that the aluminum grains are much larger in the annealed sample. The XTEM micrograph of the sample annealed at 675 °C shows that only a part of the sample surface is covered by aluminum, but there is no sign of an interaction between the layers. Figure 8 confirms the presence of big resolidified aluminum droplets on the sample surface. They are the products of the coagulation process. High-resolution cross-sectional micrographs of the $\langle\text{Si}\rangle/\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ interface before and after annealing at 675 °C are shown in Fig. 9. A very thin (about 2.5 nm) layer of SiO_2 is present in the $\langle\text{Si}\rangle/\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}/\text{Al}$ sample at the interface between silicon and the diffusion barrier. After annealing at 675 °C, all interfaces remain still atomically abrupt without any signs of compound formation or intermixing between $\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ and silicon.

IV. SUMMARY AND CONCLUSION

Amorphous Ta-Si-N alloys are exceptionally good diffusion barriers between Al and Si because it is possible to melt

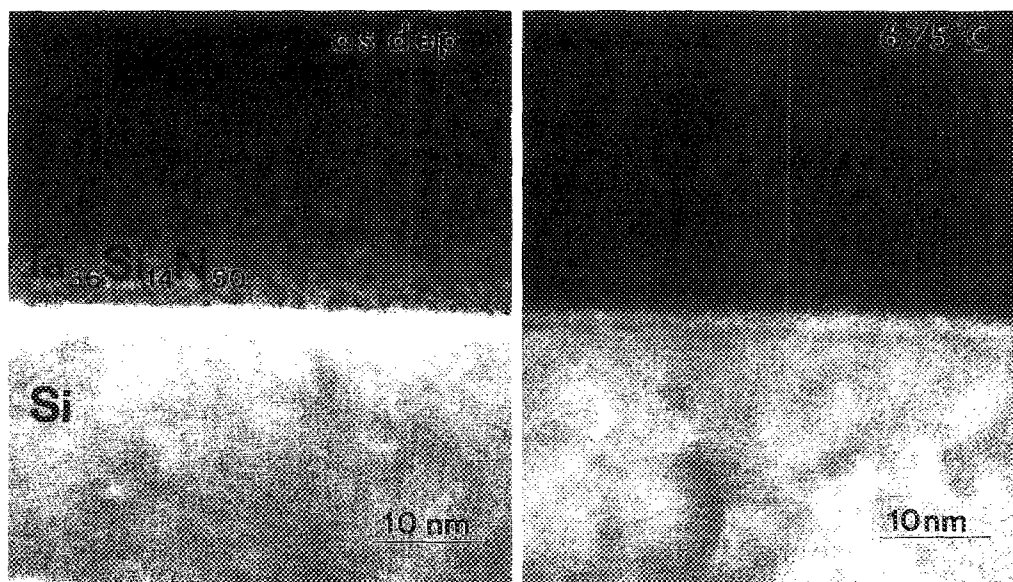


Fig. 9. High-resolution XTEM micrograph of the interface between $\langle\text{Si}\rangle$ and $\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}$ film in the as-deposited and annealed at 675 °C $\langle\text{Si}\rangle/\text{Ta}_{36}\text{Si}_{14}\text{N}_{50}/\text{Al}$ sample.

aluminum on top of the <Si>/Ta-Si-N structure without metallurgical interaction between the layers. Electrical measurements involving the <Si>/Ta-Si-N/Al metallization on shallow junctions are underway to determine if these alloys can be used in devices. These measurements are the most sensitive and relevant tool to evaluate the effectiveness of the barriers. Also the mechanism which controls the barrier performance needs to be clarified. It is possible that very thin layers of AlN and SiN develop on the interfaces between Al and Ta-Si-N and between Ta-Si-N and Si, respectively, forming a self-sealing barrier configuration like that reported for conductive oxides and nitrides diffusion barriers.¹⁸⁻²⁰ It is also possible that the Ta-Si-N alloy is itself the material responsible for the very low diffusivity of Si and Al. A combination of amorphous material properties (e.g., lack of fast diffusion paths) together with those of interstitial compounds, like W-N or TiN, may be responsible for the exceptional barrier properties of Ta-Si-N alloys. It was this notion that lead us to investigate this ternary layer in the first place.

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